



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 394 873 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
03.03.2004 Bulletin 2004/10(51) Int Cl.⁷: H01L 51/20

(21) Application number: 03254458.7

(22) Date of filing: 16.07.2003

(84) Designated Contracting States:
 AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
 HU IE IT LI LU MC NL PT RO SE SI SK TR
 Designated Extension States:
 AL LT LV MK

(30) Priority: 28.08.2002 CN 02129458

(71) Applicant: Changchun Institute of applied Chemistry Chinese Academy of Science Changchun City, Jilin Province 130022 (CN)

(72) Inventors:
 • Yan, Donghang,
 Changchun Inst. of Applied Chem.
 Changchun City Jilin Province (CN)

- Wang, Jun,
 Changchun Inst. of Applied Chemistry
 Changchun City Jilin Province (CN)
- Zhang, Jian,
 Changchun Inst. of Applied Chemistry
 Changchun City Jilin Province (CN)

(74) Representative: Chapman, Paul Gilmour et al
 Cruikshank & Fairweather,
 19 Royal Exchange Square
 Glasgow G1 3AE (GB)

(54) The field effect transistor in sandwich configuration having organic semiconductors and manufacturing process thereof

(57) A field effect transistor in sandwiched configuration having organic semiconductor, comprising: a substrate (1), a gate electrode (2) formed on the surface of the substrate (1), a gate insulation layer (3) formed on the substrate (1) and the gate insulation layer (2), which is characterized in that, further comprising: an active layer (4) formed on the gate insulation layer (3) but leaving a part of the gate insulation layer (3) to be exposed, a source and drain electrodes (5) formed on a part of the gate insulation layer (3) and a part of the active layer (4), and an active layer (6) formed on the exposed part

of the gate insulation layer (3), the active layer (4), the source electrode and the drain electrode (5). Taking full advantage of that the organic semiconductor can be processed under low temperature, the present invention adopts two or more kinds of materials to form the active semiconductor layer to make the active layer good contact with the source/drain electrode more effectively and reduce the threshold voltage of the device, and contact the semiconductor with the source/drain electrode and the insulation layer closely and tightly.

EP 1 394 873 A2

Description**FIELD OF THE TECHNOLOGY**

5 [0001] The present invention relates to a Field Effect Transistor (to be abbreviated as FET hereinafter) and manufacturing process thereof, more particularly, to a FET having a sandwich structure in which a source electrode and a drain electrode are sandwiched between semiconductors and manufacturing process thereof.

BACKGROUND OF THE TECHNOLOGY

10 [0002] In recent years, the research on organic semiconductor is exceptionally active. The performance of the organic FET is superior to that of the amorphous silicon thin film transistor (a-Si:H TFT). In particular, the mobility of some organic micro-molecule oligomers (e.g. Pentacene, Tetracene, etc.) is over 1 (square centimeter per volt per second) at room temperature. So, the organic FET is potential in such practical applications as flexural integrated circuit (to be 15 abbreviated as IC hereinafter), active matrix display and so on.

[0003] The organic FET generally adopts the bottom electrode configuration or the top electrode configuration. W099/40631 disclosed a device with a vertical geometrical configuration. Figure 1 shows the existing three geometrical 20 configurations which were applied to obtain the organic FET, wherein, 1 represents the substrate, 2 represents the gate electrode, 3 represents the insulation layer, 4 represents the active layer and 5 represents the source and drain electrodes.

[0004] The devices having a bottom electrode configuration and a vertical configurations, respectively, have the advantage of easy to be integrated and processed. But it is difficult to make the later produced organic semiconductor contact with the source and drain electrodes effectively, so that the performance of the devices having two above 25 configurations is inferior to that of the device having a top electrode configuration. Because the organic semiconductor materials are sensitive to some chemical solvents generally used in the processing of the inorganic semiconductor devices, there is difficulty in processing the device having a top electrode configuration by the conventional process for processing inorganic semiconductor devices.

[0005] The active layer of the existing organic FET is made of the material with the same molecule. US P 5,629,530 disclosed an organic FET having an active layer made of the molecules of the electron donor and receptor together. 30 Because this kind of the semiconductor applies the principle of intermingling P with N to conduct electricity, the performances of switching current ratio and mobility of the FET device with this semiconductor are very poor.

SUMMARY OF THE INVENTION

35 [0006] The objective of this invention is to provide a FET in which an active semiconductor layer contacts with the source and drain electrodes effectively. The FET shall can be easily integrated and processed.

[0007] Another objective of this invention is to provide a process for manufacturing the present FET.

[0008] To achieve these objectives, according to one aspect of the invention, there is provided a FET comprising:

40 a substrate (1),
a gate electrode (2) formed on the substrate (1),
a gate insulation layer (3) formed on the substrate (1) and the gate electrode (2),
which is characterized in that, further comprising:

45 an active layer (4) formed on the gate insulation layer (3) but leaving a part of the gate insulation layer (3) to be exposed,
a source and drain electrodes (5) formed on a part of the gate insulation layer (3) and a part of the active layer (4),
an active layer (6) formed on the exposed part of the gate insulation layer (3), the active layer (4), the source 50 electrode and the drain electrode (5).

[0009] According to another aspect of the present invention, there is provided a process for producing the present FET, comprising:

55 a. forming a layer of conducting material on a substrate and then forming a gate electrode by the method of photolithography ;
b. forming an insulation layer on the substrate and the gate electrode;
c. Vaporously depositing a semiconductor layer on a part of the insulation layer while leaving the other part of the

insulation layer exposed;

d. forming a layer of conducting material on the exposed insulation layer and the semiconductor layer, and forming a source electrode and a drain electrode by the photolithography method or delaminating method;

e. Vaporously depositing or spin-coating a semiconductor layer on the source electrode, the drain electrode, the exposed semiconductor layer and the exposed insulation layer.

5 [0010] Taking full advantage of that the organic semiconductor can be processed under low temperature, the present invention adopts two or more kinds of materials to form the active semiconductor layer, makes the active layer contact with the source/drain electrode more effectively, reduces the threshold voltage of the device, and contacts the semiconductor with the source/drain electrode and the insulation layer tightly.

BRIEF DESCRIPTION OF THE FIGURES

10 [0011]

15 Figure 1 a shows an example of the conventional FET having a top electrode geometrical configuration.

Figure 1b shows an example of the conventional FET having a bottom electrode geometrical configuration.

Figure 1c shows an example of the conventional FET having a vertical geometrical configuration.

20 Figure 2 illustrates the structure of the present sandwiched FET.

Figure 3 illustrates the application procedure of the present sandwiched FET.

25 Figure 4 shows the output characteristic curve of the present sandwiched FET in example 1, where the active layer adopts non-holonomic CuPc layer, the composite layer of CuPc and CuPc, the composite layer of NiPc and NiPc, the composite layer of CuPc and NiPc respectively.

Figure 5a shows the output characteristic curve of the present sandwiched FET in example 2, where the active 30 layer adopts the composite layer of CuPc and CuPc, the composite layer of CuPc and NdPc, the single layer of NdPc respectively.

Figure 5b shows the transfer characteristic curve of the present sandwiched FET in example 2, where the active layer adopts the composite layer of CuPc and CuPc, the composite layer of CuPc and NdPc respectively.

Figure 6 shows the output characteristic curve of the present top electrode structural device whose active layer is composed of the eutectic organic semiconductor of CuPc and NiPc.

35 [0012] Herein, "Pc" represents "phthalocyanine" and "Nc" represents "Naphthocyanine".

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

35 [0013] The present invention will be described with reference to the accompanying drawings.

40 [0014] Figure 2 illustrates the structure of the present sandwiched FET. The conducting material layer is set on the substrate (1) to form the gate electrode (2). The insulation material is set on the substrate and the gate electrode to form the gate insulation layer (3). The hole semiconductor is set on the gate insulation layer to form part of the active layer (4). The conducting material is set on the hole semiconductor layer and the gate insulation layer to form the source and drain electrode (5). In addition, together with the hole semiconductor, part of the semiconductor (6) is set on the gate insulation layer, the semiconductor layer, the gate of the source electrode and the drain electrode to form the active layer.

45 [0015] According to one example of the present invention, the eutectic and laminate structure of the existing model P type semiconductor CuPc and NiPc is adopted to form a kind of active semiconductor. Compared with a single kind of material, this active semiconductor's current on/off ratio has no obvious loss, while its threshold voltage has been reduced markedly and its carrier mobility has been greatly improved. The principle is that a semiconductor made of the mixture, eutectic and laminate of several kinds of material have good contact with the surfaces of the source and drain electrodes than the semiconductor made of a single kind of material does.

50 [0016] According to one example of the present invention, the laminate structure of the existing model P type semiconductor CuPc and the resistance material NdPc₂ is adopted to form a kind of active semiconductor. Compared with a single kind of material, this active semiconductor's switching current ratio and carrier mobility have been greatly improved, while its threshold voltage has been reduced markedly. The principle is that a semiconductor formed by laminating two kinds of material have good contact with the surfaces of the source and drain electrodes than CuPc does. Meanwhile, the field effect transmission property of CuPc is enhanced by NdPc₂.

55 [0017] Figure 6 also shows the output characteristic curve of the CuPc/NiPc eutectic FET. When V_G equals to -30V, the FET's hole carrier mobility is 0.04 cm²/V.s in the saturation region, and its current on/off ratio is 4x10⁵, and the threshold voltage is -8V.

[0018] The organic semiconductor of the present invention is made of the mixture, eutectic and laminate of various molecular materials. Compared with the device made of a single material, the properties of this FET, such as, the mobility, the threshold and the switching current ratio are improved markedly.

[0019] Now the present invention will be further illustrated with reference to the following examples.

5

Example 1:

[0020] Copper phthalocyanine (CuPc), zinc phthalocyanine (ZnPc), nickel phthalocyanine (NiPc), cobalt phthalocyanine (CoPc), H₂Pc, TiOPc, VOPc and Pentacene used in this example were commercial products, and they were sublimated and purified before being used.

[0021] On the 7059 glass substrate or the flexible plastic substrate 1, a film layer of metal Ta with about 200 nm in thickness was plated by using the radio frequency (RF) magnetism controlled sputtering method and shaped into the gate electrode 2 by the photolithography method. On the grid electrode, a film layer of Ta₂O₅ with a thickness of about 100 nm was reactively sputtered as the gate insulation layer 3 by the direct current (DC) magnetism controlled sputtering method. Then depositing CuPc using the molecular vapor phase deposition method to prepare the active layer 4 having a thickness of about 20 nm. Subsequently, using Au to prepare the source electrode and the drain electrode 5 with a thickness of about 50 nm. Finally, depositing one selected from a group consisting of CuPc, ZnPc, NiPc, CoPc, H₂Pc, TiOPc, VOPc or Pentacene using the molecular vapor phase deposition method to form the active layer 6 having a thickness of about 30nm.

[0022] Figure 4 shows the output characteristic curve of the FET sandwiched with CuPc but having no active layer 6 when V_G is -30V. From it, no obvious field effect was observed.

[0023] Figure 4 shows the output characteristic curve of the CuPc/CuPc sandwich FET when V_G is -30V. The FET's hole carrier mobility is 0.01 cm²/V.s in the saturation region, its threshold voltage is -18V, and its current on/off ratio is 4x10⁴.

[0024] Figure 4 also shows the output characteristic curve of the NiPc/NiPc sandwich FET when V_G is -30V. The FET's hole carrier mobility is 0.005 cm²/V.s in the saturation region, its current on/off ratio is 4x10⁴ and its threshold voltage is -16V when V_G is -30V.

[0025] Figure 4 also shows the output characteristic curve of the CuPc/NiPc sandwich FET when V_G is -30V. The FET's hole carrier mobility is 0.01 cm²/V.s in the saturation region, its current on/off ratio is 4x10⁵ and its threshold voltage is -13.5V when V_G is -30V.

[0026] Compared with the CuPc/CuPc sandwich FET and the NiPc/NiPc sandwich FET, the CuPc/NiPc sandwich FET presents no obvious variation in the switching current ratio, but its threshold voltage is obviously reduced. Table 1 lists the performance parameters of the existing organic sandwich FET, in which, the mobility and threshold voltage are determined when V_G equals to -30V.

35

Table 1

| Semiconductor 4 | Semiconductor 6 | Hole mobility cm ² /V.s | Threshold Voltage -V |
|----------------------|-------------------|------------------------------------|----------------------|
| CuPc | CuPc | 0.01 | 18 |
| NiPc | NiPc | 0.005 | 16 |
| CuPc | NiPc | 0.01 | 13.5 |
| CuPc/NiPc (eutectic) | | 0.04 | 8 |
| CuPc | ZnPc | 0.006 | 5 |
| CuPc | CoPc | 0.003 | 11 |
| CuPc | H ₂ Pc | 0.007 | 17 |
| CuPc | TiOPc | 0.009 | 17 |
| CuPc | VOPc | 0.01 | 15 |
| CuPc | Pentacene | 0.01 | 8 |

50

Example 2:

[0027] All the twin-Pc metals (e.g. LaPc₂, CePc₂, PrPc₂, NdPc₂, SmPc₂, EuPc₂, GdPc₂, DyPc₂, HoPc₂, ErPc₂, TmPc₂, YbPc₂, LuPc₂, YPc₂, ZrPc₂, HfPc₂, SnPc₂), H₂Nc, CoNc, CuNc, ZnNc and NiNc used in the present example were synthesized by the methods discussed in the following references: (1) J. Jiang, R. C. W. Liu, T. C. W. Mack, T. D. W. Chan, D. K. P. Ng, *Polyhedron*, 1997, 16, 515; (2) W. Liu, J. Jiang, D. Du, D. P. Arnold, *Aust. J. Chem.*, 2000, 53, 131; (3) R. Polley, M. Hanack, *J. Org. Chem.*, 1995, 60, 8278; (4) M. hanack, R. Polley, S. Knecht, U. Schlick, *Inorg. Chem.*, 1995, 34, 3621; (5) M. L. Kaplan, A. J. Lovinger, W. D. Reents, jun, P. H. Schmidt, *Mol. Cryst. Liq. Cryst.*,

1984, 112, 345. They were sublimated and purified before being used.

[0028] On the 7059 glass substrate or the flexible plastic substrate 1, a film layer of metal Ta with about 200 nm in thickness was plated by using the radio frequency (RF) magnetism controlled sputtering method and shaped into the gate electrode 2 by the photolithography method. On the gate electrode, a film layer of Ta_2O_5 with a thickness of about 100 nm was reactively sputtered as the gate insulation layer 3 by the direct current (DC) magnetism controlled sputtering method. Then depositing CuPc using the molecular vapor phase deposition method to prepare the active layer 4 having a thickness of about 20 nm. Subsequently, using Au to prepare the source electrode and the drain electrode 5 with a thickness of about 50 nm by the photolithography technology. Finally, depositing one selected from a group consisting of twin-Pc metals ($LaPc_2$, $CePc_2$, $PrPc_2$, $NdPc_2$, $SmPc_2$, $EuPc_2$, $GdPc_2$, $TbPc_2$, $DyPc_2$, $HoPc_2$, $ErPc_2$, $TmPc_2$, $YbPc_2$, $LuPc_2$, YPC_2 , $ZrPc_2$, $HfPc_2$, $SnPc_2$), H_2Nc , $CoNc$, $CuNc$, $ZnNc$ and $NiNc$ using the molecular vapor phase deposition method to form the active layer 6 having a thickness of about 30nm.

[0029] Figure 5 shows the transfer characteristic curves of the NdNc top electrode FET and the NdNc sandwich FET. From it, we can see that the NdNc top electrode FET presents no field effect, while the NdNc sandwich FET presents steady field effect. When V_G is -30V, the NdNc sandwich FET's hole mobility in the saturation region is $0.05\text{cm}^2/\text{V.s}$ and the threshold voltage is -12V. Table 2 lists the performance parameters of the FET sandwiched new organic semiconductor, in which case, the mobility is under the constraint that V_G equals to -30V.

Table 2

| | Semiconductor 4 | Semiconductor 6 | Hole mobility $\text{cm}^2/\text{V.s}$ |
|----|-----------------|-----------------|--|
| 20 | CuPc | $LaPc_2$ | 0.02 |
| | CuPc | $CePc_2$ | 0.017 |
| | CuPc | $PrPc_2$ | 0.025 |
| | CuPc | $NdPc_2$ | 0.015 |
| 25 | CuPc | $SmPc_2$ | 0.01 |
| | CuPc | $EuPc_2$ | 0.03 |
| | CuPc | $GdPc_2$ | 0.025 |
| | CuPc | $TbPc_2$ | 0.009 |
| 30 | CuPc | $DyPc_2$ | 0.02 |
| | CuPc | $HoPc_2$ | 0.01 |
| | CuPc | $ErPc_2$ | 0.05 |
| | CuPc | $TmPc_2$ | 0.03 |
| 35 | CuPc | $YbPc_2$ | 0.03 |
| | CuPc | $LuPc_2$ | 0.07 |
| | CuPc | YPC_2 | 0.05 |
| | CuPc | $ZrPc_2$ | 0.06 |
| 40 | CuPc | $HfPc_2$ | 0.02 |
| | CuPc | $SnPc_2$ | 0.007 |
| | CuPc | H_2Nc | 0.01 |
| | CuPc | $CoNc$ | 0.08 |
| | CuPc | $CuNc$ | 0.02 |
| 45 | CuPc | $ZnNc$ | 0.05 |
| | CuPc | $NiNc$ | 0.02 |

Example 3:

[0030] $F_{16}CuPc$ and $F_{16}ZnPc$ used in the present experiment are commercial products, which have been sublimated and purified before being used.

[0031] On the 7059 glass substrate or the flexible plastic substrate 1, a film layer of metal Ta with about 200 nm in thickness was plated by using the radio frequency (RF) magnetism controlled sputtering method and shaped into the gate electrode 2 by the photolithography method. On the gate electrode, a film layer of Ta_2O_5 with a thickness of about 100 nm was reactively sputtered as the gate insulation layer 3 by the direct current (DC) magnetism controlled sputtering method. Then depositing $F_{16}CuPc$ using the molecular vapor phase deposition method to prepare the active layer 4 having a thickness of about 20 nm. Subsequently, using Au to prepare the source electrode and the drain electrode 5 with a thickness of about 50 nm by the photolithography technology. Finally, depositing $F_{16}ZnPc$ using the

molecular vapor phase deposition method to form the active layer 6 having a thickness of about 30nm. The electron mobility of the sandwich field effect devices is $0.02\text{cm}^2/\text{V.s}$ in the saturation region. The electron mobility of the F_{16}CuPc and F_{16}ZnPc sandwich FET is $0.016\text{cm}^2/\text{V.s}$ in the saturation region.

5 [0032] The present invention has been described by way of the above examples. The present invention is not limited to the modes described in the respective examples but naturally includes various other modes according to the principle of the present invention. In general, the sandwich FET according to the present invention can be processed to the elements of the 2D and 3D integrated devices. These integrated devices can be applied in flexible IC, the active matrix display and the like. The FET according to the present invention can be processed at low temperature. Besides the traditional photoetching, many methods such as mimeograph, printing and the like can be used to prepare the bipolar 10 type FET of the present invention.

Claims

15 1. A field effect transistor sandwiched organic semiconductor, comprising:

20 a substrate (1),
a gate electrode (2) formed on the surface of the substrate (1),
a gate insulation layer (3) formed on the substrate (1) and the gate insulation layer (2),
which is **characterized in that**, further comprising:

25 an active layer (4) formed on the gate insulation layer (3), or meanwhile leaving a part of the gate insulation layer (3) to be exposed,
a source and drain electrodes (5) formed on a part of the gate insulation layer (3) and a part of the active layer (4),
an active layer (6) formed on the exposed part of the gate insulation layer (3), the active layer (4), the source electrode and the drain electrode (5).

30 2. The field effect transistor according to claim 1, wherein the said active layer has holes.

35 3. The field effect transistor according to claim 2, wherein the said semiconductor material is organic semiconductor material or the hybridized product of organic material and inorganic material.

40 4. The field effect transistor according to claim 3, wherein the said organic semiconductor material is a solid-state material formed by mixing, eutecting or laminating of two or more kinds of molecular material.

45 5. The field effect transistor according to claim 4, wherein the said organic semiconductor material has a carrier mobility of at least $10^{-3}\text{cm}^2/\text{V.s}$.

6. The field effect transistor according to claim 1, wherein the said semiconductor material for the active layer (4) is the same as that for the active layer (6).

7. The field effect transistor according to claim 1, wherein the said semiconductor material for the active layer (4) is different from that for the active layer (6).

50 8. The field effect transistor according to claim 1, wherein the said semiconductor material for the active layers (4) and (6) is eutectic.

9. The field effect transistor according to claim 1, wherein the said active layers (4) and (6) are comprised of at least one selected from a group consisting of CuPc, NiPc, ZnPc, H₂Pc, TiOPc, VOPc, F_{16}CuPc , F_{16}ZnPc and Pentacene, respectively.

55 10. The field effect transistor according to claim 1, wherein the said active layer (4) is comprised of at least one selected from a group consisting of CuPc, NiPc, ZnPc, H₂Pc, F_{16}CuPc , F_{16}ZnPc and Pentacene, and the said active layer (6) is comprised of at least one selected from a group consisting of twin-Pc metal, H₂Nc, CoNc, CuNc, ZnNc and NiNc.

11. The field effect transistor according to claim 10, wherein the said twin-Pc metal is at least one selected from a

group consisting of LaPc_2 , CePc_2 , PrPc_2 , NdPc_2 , SmPc_2 , EuPc_2 , GdPc_2 , TbPc_2 , DyPc_2 , HoPc_2 , ErPc_2 , TmPc_2 , YbPc_2 , LuPc_2 , YPc_2 , ZrPc_2 , HfPc_2 and SnPc_2 .

12. A process for producing a field effect transistor sandwiched an organic semiconductor, comprising:

5

- a. forming a layer of conducting material on a substrate and then forming a gate electrode by the method of photolithography;
- b. forming an insulation layer on the substrate and the gate electrode;
- c. vaporously depositing a semiconductor layer on a part of the insulation layer while leaving the other part of the insulation layer exposed;
- 10 d. forming a layer of conducting material on the exposed insulation layer and the semiconductor layer, and forming a source electrode and a drain electrode by the photolithography method or delaminating method;
- e. vaporously depositing or spin-coating a semiconductor layer on the source electrode, the drain electrode, the exposed semiconductor layer and the exposed insulation layer.

15

20

25

30

35

40

45

50

55

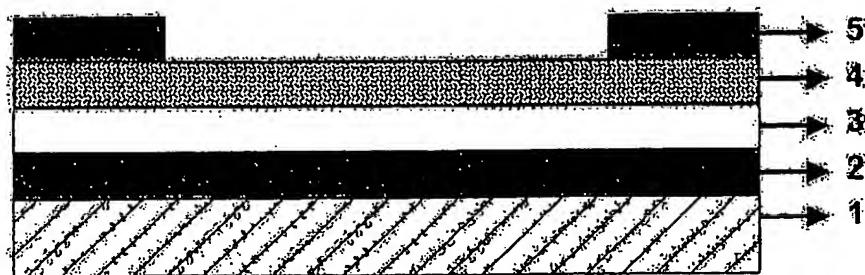


Fig.1a

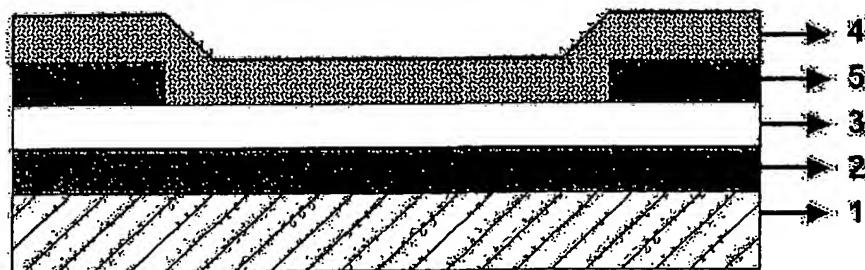


Fig.1b

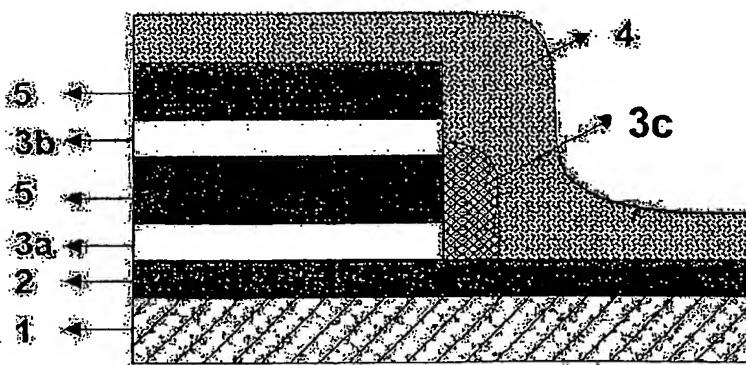


Fig.1c

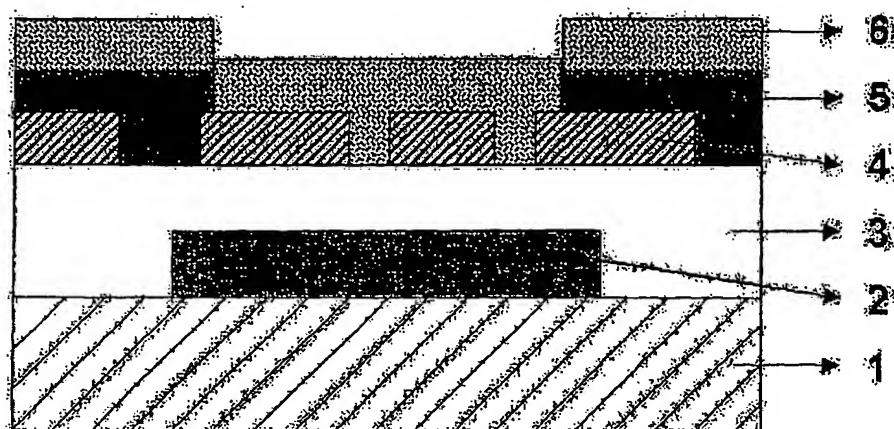


Fig.2

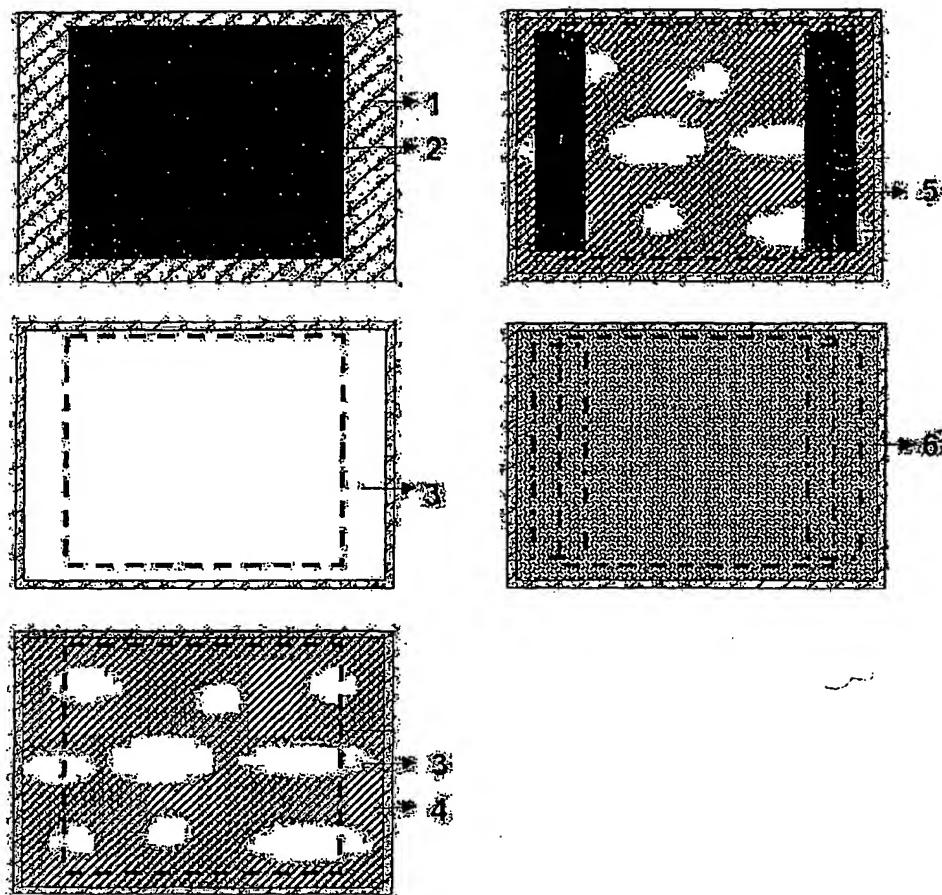


Fig.3

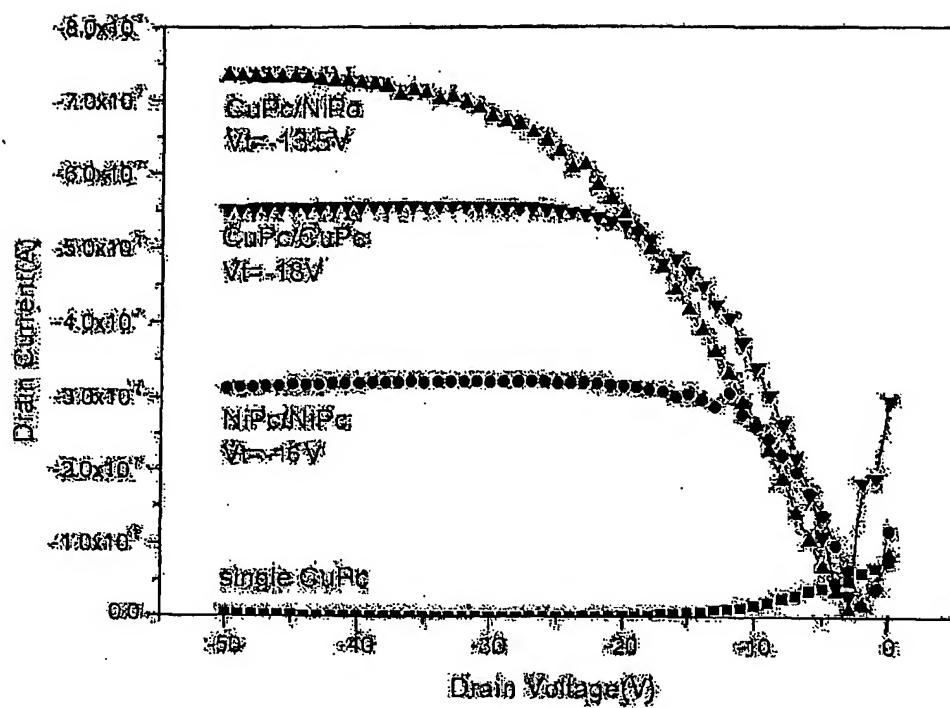


Fig.4

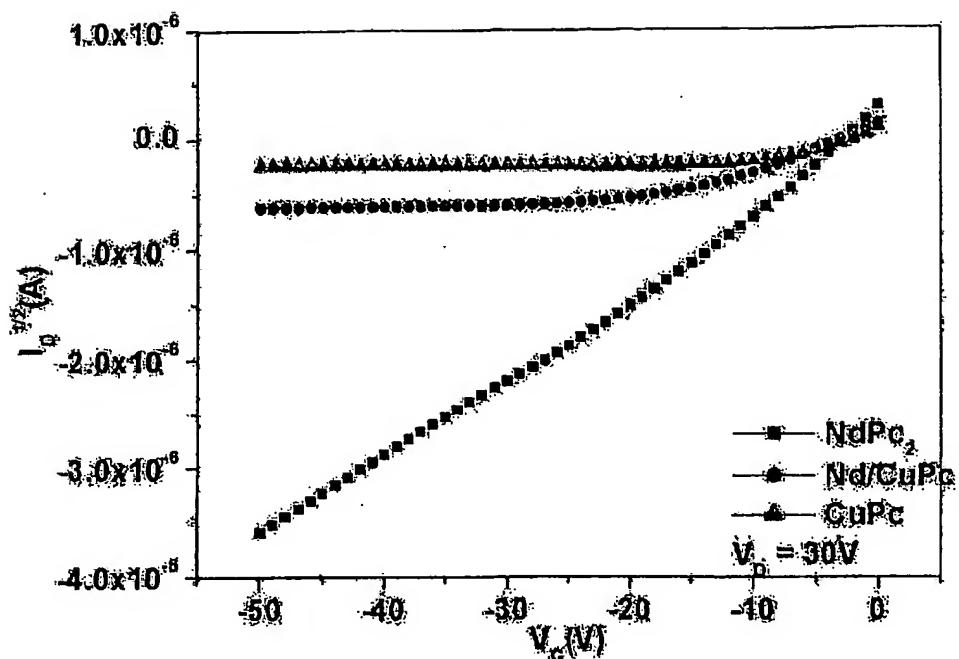


Fig.5a

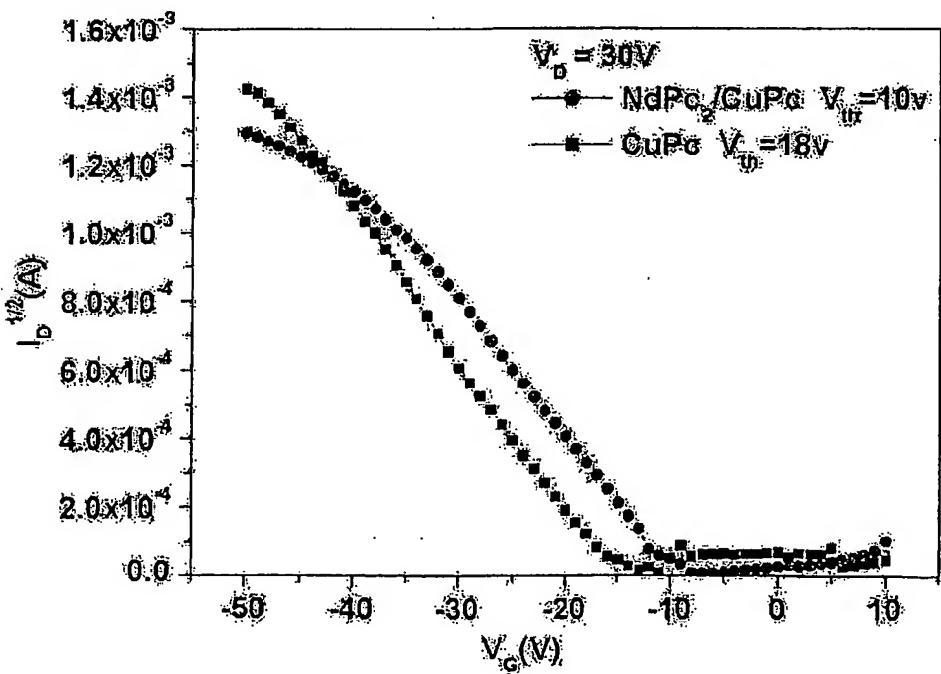


Fig.5b

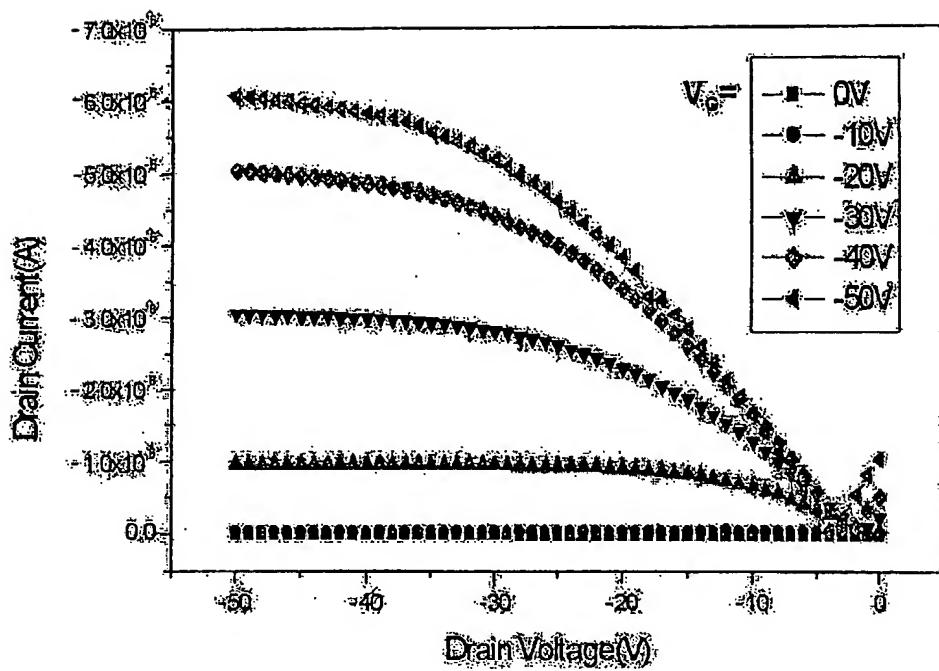


Fig.6